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Technical Report

to the

Office of Naval Research

on

The Electrochemical Polarization of Zirconium
in Distilled   Water

by

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Austin, Texas

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Summary

The cathodic polarization curve for zirconium in air saturated distilled water at 40°C. was determined in the current density range 3.0×10^{-7} to 1.0×10^{-3} amp./cm.^{2}.

At low current densities the reaction was the reduction of dissolved molecular oxygen to hydroxyl ions, its limiting diffusion current being about 5×10^{-6} amp./cm.^{2}. The formation of a zirconium hydride film was the reaction proposed to explain a plateau in the curve which had a constant potential of -0.30 volts vs. S. C. E. and a limiting current of 1.0×10^{-4} amp./cm.^{2}. X-ray diffraction data, time-potential curves, observations and other evidences substantiated this possibility. Above 1.0×10^{-4} amp./cm.^{2} hydrogen evolution occurred and the curve followed a Tafel relationship, the slope being -0.14 volts. The hydrogen overvoltage at 1.0 ma./cm.^{2} was 0.75 volts.

The open circuit potential of zirconium in air saturated water at 40°C. was determined to be +0.16 volts vs. S. C. E.

The anodic polarization curve for zirconium in air saturated
distilled water at 40°C. was determined in the current density
range from 1.0×10^{-5} to 3.0×10^{-3} amp./cm.^{2}.   The potential
rose in a linear fashion with the logarithm of current density,
the slope being 0.07 volts.   A small amount of corrosion which
increased with temperature was observed but not explained.

INTRODUCTION

Previous studies (1) showed that zirconium pitted in sodium chloride solution during anodic polarization under certain conditions. Earlier work also showed an unexplained plateau at rather low current densities for both zirconium and titanium in the NaCl solutions (1),(2). The purpose of the present study was to follow the effects of applied current on zirconium when immersed in distilled water.

The apparatus used in the previous work was employed here in almost the same form and need not be described again.

Materials

Two zirconium sheets 31.5 x 4.6 x 0.3 cm. were kindly supplied by the Argonne National Laboratory and pieces 0.5 by 1.5 cm. were cut from these. Analysis of the metal as determined by the National Spectrographic Laboratories, Inc., Cleveland is as follows (all percentages standing alone are approximate): Fe 0.02%; Hf < 0.03%; Si < 0.001%; Al 0.01-0.02%; Cu < 0.001%; Ti 0.002%; Mn < 0.001%; Mg 0.005-0.01%; Pb < 0.003%; Mo < 0.001%; Ni 0.003%; Cr 0.002%; Sn < 0.01%; Na < 0.01%; Ba < 0.01%; Bi, Cb, Ta not detected.

The coupons were buffed on number 2 emery paper and finished on number 2/0, then degreased by wiping clean with lens paper wet with ethanol and polishing with clean, dry, lens paper.

A small square of celluloid with a hole previously punched in it was laid on the polished coupon. Small drops of Ucilon lacquer were placed around the outer edge of the celluloid. These spread between the celluloid and zirconium by capillary action, thereby sealing the celluloid to the coupon and leaving a reproducible circular area of 0.35 ± 0.01 cm.^{2}. The coupon was then placed in its holder and all but the masked off circular area coated with ceresin wax.

The distilled water was prepared in the following manner. Once distilled water was redistilled from alkaline permanganate and then redistilled from dilute sulfuric acid, the first and last twenty-five percent being discarded. The specific conductance of water obtained by this procedure ran consistently about 2×10^{-6} ohm^{-1}. The water was stored in pyrex bottles which had been previously leached for at least thirty days with water of approximately the same conductivity.

Some of this water was pre-electrolyzed between spectroscopically pure carbon electrodes for long periods at potentials just short of that required for gas evolution. Results obtained with the water distilled as described were the same as those obtained with the water which had been distilled and pre-electrolyzed.

Mercury used in the preparation of saturated calomel electrodes was redistilled in a vacuum. All other reagents used were C. P. analytical grade.

Measurements

Each zirconium coupon was mounted in a lucite holder, similar to one already described (1), along with a platinum polarizing electrode and a saturated calomel half cell. The potentiometer was connected across a calibrated resistor and set at the calculated value for IR drop to give the desired current. Voltage from a power supply* through dropping resistors was then varied until there was no deflection of the galvanometer. On measuring the electrode potentials a thermionic amplifier (2) was switched into the circuit so that the current drawn into the measuring circuit was of the order of 10^{-12} amps.

All potentials given are relative to the saturated calomel electrode, and those used in plotting the polarization curves are steady values, i.e., constant for at least twelve hours. The convention used is that the more negative values are more anodic; decrease in potential means change to more negative values. All polarization measurements were made at $40° \pm 1°C$. Polarization of the coupons at one current density in most instances did not influence the steady potential attained by that coupon at another current density so in some cases the same coupon was polarized at more than one current density.

RESULTS

Effect of Solution Resistance

The position of the calomel electrode relative to the polarized electrode had a marked effect on the measured potential when the polarizing current density was in excess of 0.1 ma./cm.^{2}. The variation is caused in part by the IR drop of the solution and in part by the disturbance in current distribution to the zirconium by blockage because of the reference electrode. Without accurate knowledge of the current distribution through the solution it is not possible to calculate the necessary correction so it was determined experimentally.

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*The power supply was built by Sherman Kottle of these laboratories. The authors are happy to acknowledge his help in this matter.

A saturated calomel electrode was arranged on a lucite rack which was made so as to permit measured movement of the electrode. The potential was measured as a function of distance of electrode tip from the coupon. Starting with the electrode tip at 1.5 to 2.0 cm. distance the potential was found to vary linearly with distance toward the coupon down to a point which depended on the current, being closer the smaller the current. Up to this point it is considered that the only correction necessary is that for the solution IR drop. That is, current blockage is not important unless the tip was moved closer. Extrapolation of the linear portion to zero distance was then taken as the actual polarized potential, All measurements were made with the tip of the reference electrode 1.0 cm. from the coupon and corrections were made for IR drop where they were significant. Figure 1 gives curves typical of the variation of measured potential with distance from coupon at several current values.

Effect of Current Flow on pH

The pH values of the solutions were measured before and after each run and variations of not more than 0.3 to 0.6 pH unit were found. The solutions were well agitated and the method of stirring was such as to permit the belief that there was little difference in pH of the solution adjacent to the coupon and that in the bulk of the solution. Several experiments were run in an attempt to determine the pH of the adjacent liquid film and in no case was a difference found. However, no firm claim is made that these experiments permitted close enough approach to the coupon surface. In one case a wick was used, in another a very small glass electrode was used, and several attempts were made to sample the 'liquid film' in question.
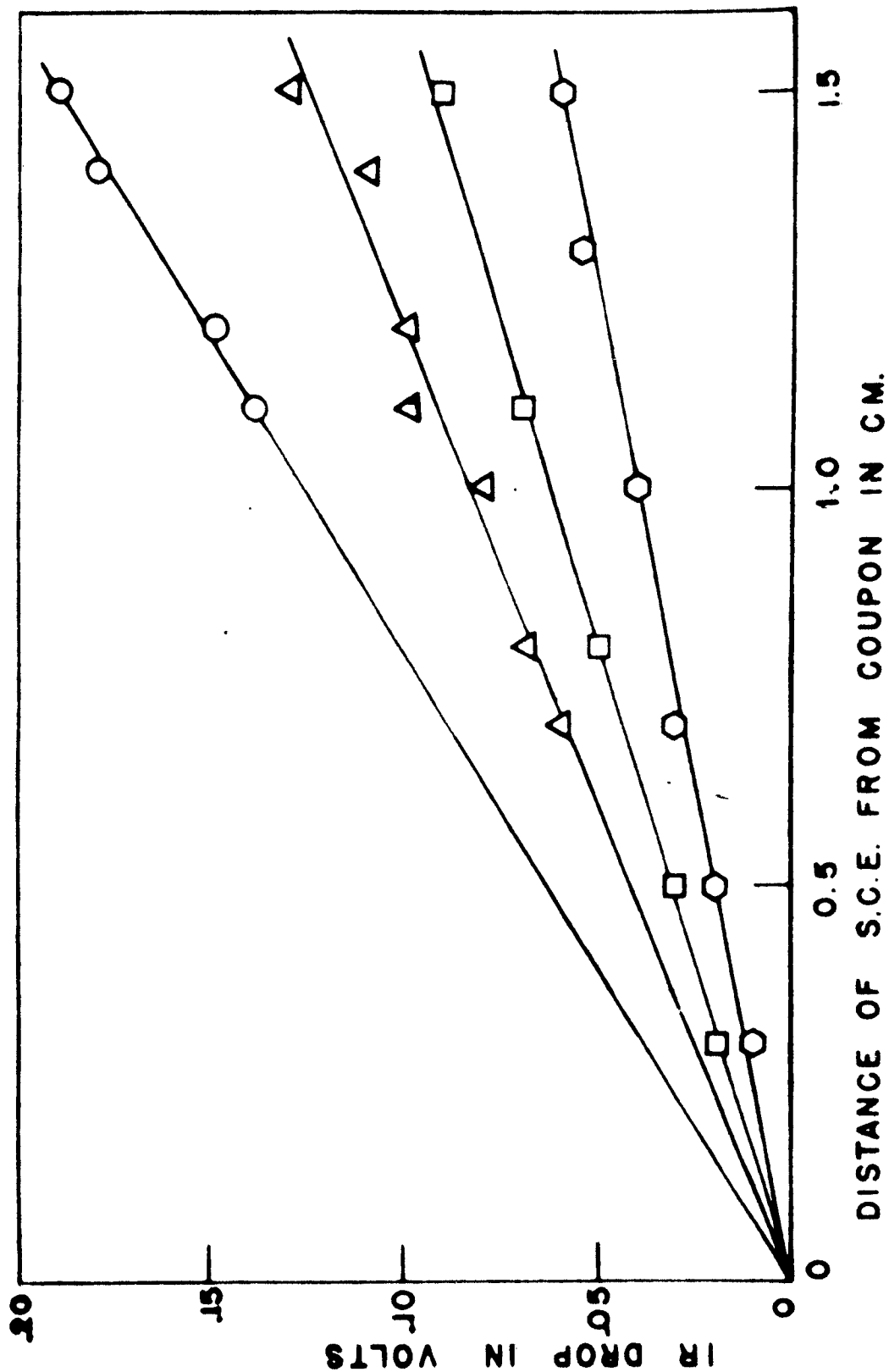
Cathodic Polarization

The cathodic polarization curve for zirconium in air saturated distilled water at $40 \pm 1^\circ$C. was determined in the current density range of 3.0×10^{-7} to 1.0×10^{-3} amp./cm.^{2}. Air was constantly circulated over the surface and since the solutions were being continuously agitated it is assumed that the solutions were saturated with air. The results are given in Table I and are shown in Figure 2. Since the current scale is logarithmic it is not possible to show the open circuit potential of zirconium. This potential was measured several times and the values obtained ranged from +0.14 to +0.18 volts vs. S. C. E., with an average value of +0.16.

The points shown in Figure 2 are the result of polarization measurements on eighteen different coupons cut from the same sheet of zirconium. Usually a coupon was polarized at one current density for the entire run, but a few points were obtained by polarizing a coupon already at a constant potential at a higher current density.

FIGURE 1

The variation of solution IR drop with distance of the saturated calomel electrode tip from the coupon surface at the following currents

O 3.5×10^{-4} amp.

△ 2.8×10^{-4} amp.

□ 1.75×10^{-4} amp.

◯ 1.05×10^{-4} amp.

DISTANCE OF S.C.E. FROM COUPON IN CM.

IR DROP IN VOLTS

TABLE I

Data for the cathodic polarization of zirconium in air saturated
distilled water at 40°C.

Current Density (amp./cm.^{2}.)	Potential (volts vs. S. C. E.)	
	Increasing Current Density	Decreasing Current Density
0.00	+0.16	---
3.0×10^{-7}	+0.14	---
5.0×10^{-7}	+0.12	---
1.0×10^{-6}	---	+0.14
2.0×10^{-6}	+0.06	-0.08
3.0×10^{-6}	-0.07	---
4.0×10^{-6}	-0.10	---
5.0×10^{-6}	-0.20	-0.32
1.0×10^{-5}	-0.29	---
2.0×10^{-5}	-0.30	-0.33
3.0×10^{-5}	-0.28	---
5.0×10^{-5}	-0.30	-0.33
7.0×10^{-5}	-0.44	-0.44
1.0×10^{-4}	-0.67, -0.64	---
1.5×10^{-4}	-1.11	---
2.0×10^{-4}	-1.28	---
3.0×10^{-4}	-1.34	---
4.0×10^{-4}	-1.38	---
5.3×10^{-4}	-1.36	---
7.0×10^{-4}	-1.41	---
1.0×10^{-3}	-1.41	---

FIGURE 2

Cathodic polarization curve for zirconium in air saturated
distilled water at 40°C.

        O   increasing current density

        △   decreasing current density
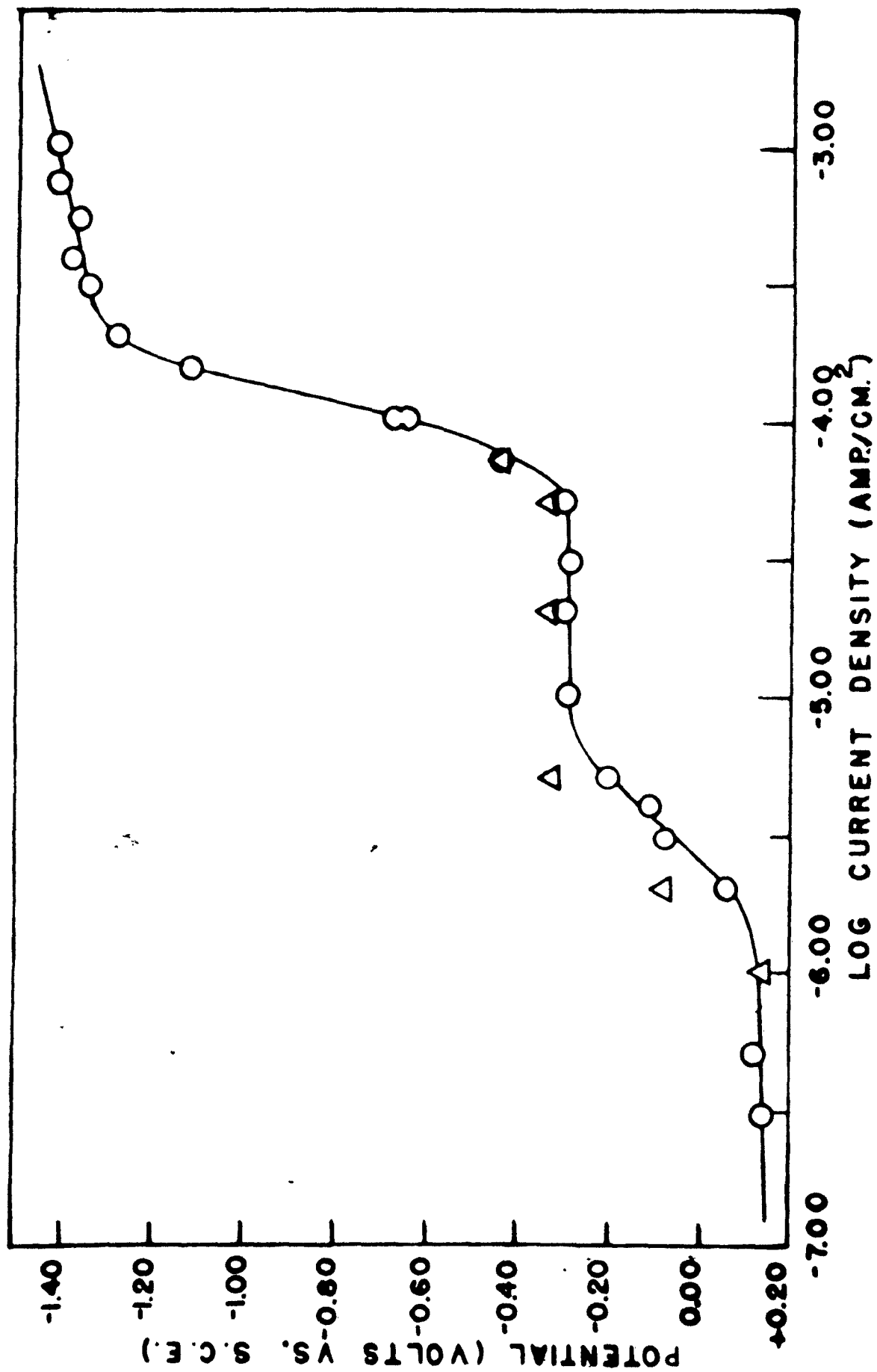
Considerable care was exercised in determining this curve and enough points were taken so that all regions could be drawn in detail. The fact that a smooth curve is the result indicates that no appreciable error was introduced by using different coupons prepared in the same way. Perhaps the greatest error was encountered at current densities greater than 1.0 ma./cm.^{2}. At these higher current densities adjustment of the polarizing current was more difficult because the ratio of IR drop in the circuit proper to the IR drop in the solution was so small that slight changes in solution resistance had an appreciable effect on the polarizing current. Also in this region the potentials had a tendency to fluctuate, making it necessary to record average values in many cases.

There are five distinct regions of the polarization curve. An initial portion, linear with the logarithm of current density and of small slope, followed by a rapid decrease in potential beginning at about 1.5×10^{-6} amp./cm.^{2}. This levels off at about 7.0×10^{-6} amp./cm.^{2} to give a flat region at a potential of -0.30 volts. Another rapid decrease in potential is noted about 1.0×10^{-4} amp./cm.^{2} which levels off to a linear decrease. The slope in this region is 0.135 volts as determined from the plot.

The surfaces of coupons polarized at current densities in the three upper regions of the curve were covered with a black, hard, adherent film which was difficult to remove. The extent of film formation increased with current density, the coupons from the region of highest current density all bearing about the same amount of film and being very black. The film on coupons from the plateau beginning at 7×10^{-6} amp./cm.^{2} was very slight and at the lower currents was noticeable only by comparison with a coupon polarized at a still lower current density. The surface was, however, uniformly covered with film even at the low current densities.

Gaseous evolution from the coupon surface was not observed until the highest current density region was reached.

A coupon which has been polarized in the highest region does not retrace the curve exactly when the current is reduced. For example, the plateau starting at 7×10^{-6} amp./cm.^{2} occurs at a slightly lower potential, -0.33 volts, than does that obtained with fresh coupons or that observed by approaching from low current densities. Also the first potential fall occurs at a lower density when the measurements are made by reducing the current. Six coupons previously polarized at high currents were repolarized in the range of current densities governing these two regions and the points obtained are shown by triangles in Figure 2. Hysteresis appears to be significant only in these two regions.

Cathodic Time-Potential Studies

Before the beginning of one run the coupons were permitted to stand in distilled water until they reached the open circuit potential. The time required for this was approximately one week. The polarizing current was then begun and the potentials recorded at various time intervals. The data for this study may be found in Table II and the resulting charging curves are shown in Figure 3.

The curves represented by diamonds and hexagons are for the current densities 3.0×10^{-7} amp./cm.^{2} and 3.0×10^{-6} amp./cm.^{2}, respectively, and are from the first two regions of the polarization curve, the initial, linear, slow decrease in potential at low current density and the first rapid decrease in potential. These curves show the change from open circuit value (0.16 v) to the steady potential takes place in one hour. At 1.0×10^{-5} amp./cm.^{2}, which is at the beginning of the third region, the flat portion at the potential -0.30 volts. A minimum (i.e., most negative value) is noted after about three hours which is followed by a steady increase in potential to the steady value. The greater the current density, the earlier the minimum shows up and at current densities in the fourth region, the second rapid decrease, the minimum cannot be observed at all. This latter region furnished the curve at current density 1.0×10^{-4} amp./cm.^{2}, the points of which are represented by circles. For one point in this fourth region a potential measurement was made after one minute and the minimum had already been passed. It was not possible to manipulate the apparatus rapidly enough to get a potential measurement in less than one minute.

If the coupons are not allowed to come to the open circuit potential before starting the polarizing current, the charging curves for the two lower current density regions show a gradual increase in potential from an initially more negative value to the constant polarized value in a period of about 75 hours. No change in appearance of the other curves occurs.

For the charging of coupons polarized at the highest current densities used, the potential decreases rapidly to the constant value, usually in about two to three hours.

Anodic Polarization

The anodic polarization curve for zirconium in air saturated distilled water was determined in the current density range 1.0×10^{-5} to 3.0×10^{-3} amp./cm.^{2} and is shown in Figure 4 and the data are given in Table III. The points are from seven different coupons held at the desired current density for the entire run. The curve shows a linear increase in potential with the logarithm of current density, the slope of the line being 0.070 volts per log unit.

TABLE II

Data for the variance of potential with time for the cathodic polarization of zirconium in air saturated distilled water at 40°C.

<u>Potential (volts vs. S. C. E.)</u>

Time (hours)	Current Density (amp./cm.^{2}.)			
	3.0×10^{-7}	3.0×10^{-6}	1.0×10^{-5}	1.0×10^{-4}
1.0	0.14	-0.05	-0.37	-0.87
1.5	0.14	-0.05	-0.44	-0.84
2.0	0.14	-0.05	-0.56	-0.83
2.8	0.14	-0.05	-0.57	-0.81
5.2	0.14	-0.05	-0.56	-0.76
18.2	0.14	-0.05	-0.47	-0.72
20.0	0.14	-0.05	-0.44	-0.71
23.8	0.14	-0.05	-0.42	-0.70
26.2	0.14	-0.05	-0.41	-0.70
30.0	0.14	-0.06	-0.37	-0.69
41.5	0.14	-0.07	-0.30	-0.67
43.0	0.14	-0.07	-0.29	-0.67
46.3	0.13	-0.07	-0.29	-0.67
48.0	0.14	-0.07	-0.29	-0.67
49.5	0.14	-0.07	-0.29	-0.67
54.0	0.14	-0.07	-0.29	-0.67

FIGURE 3

Time-potential curves for the cathodic polarization of zirconium in air saturated distilled water at the following current densities

◇ 3.0×10^{-7} amp./cm.^{2}

◌ 3.0×10^{-6} amp./cm.^{2}

△ 1.0×10^{-5} amp./cm.^{2}

○ 1.0×10^{-4} amp./cm.^{2}
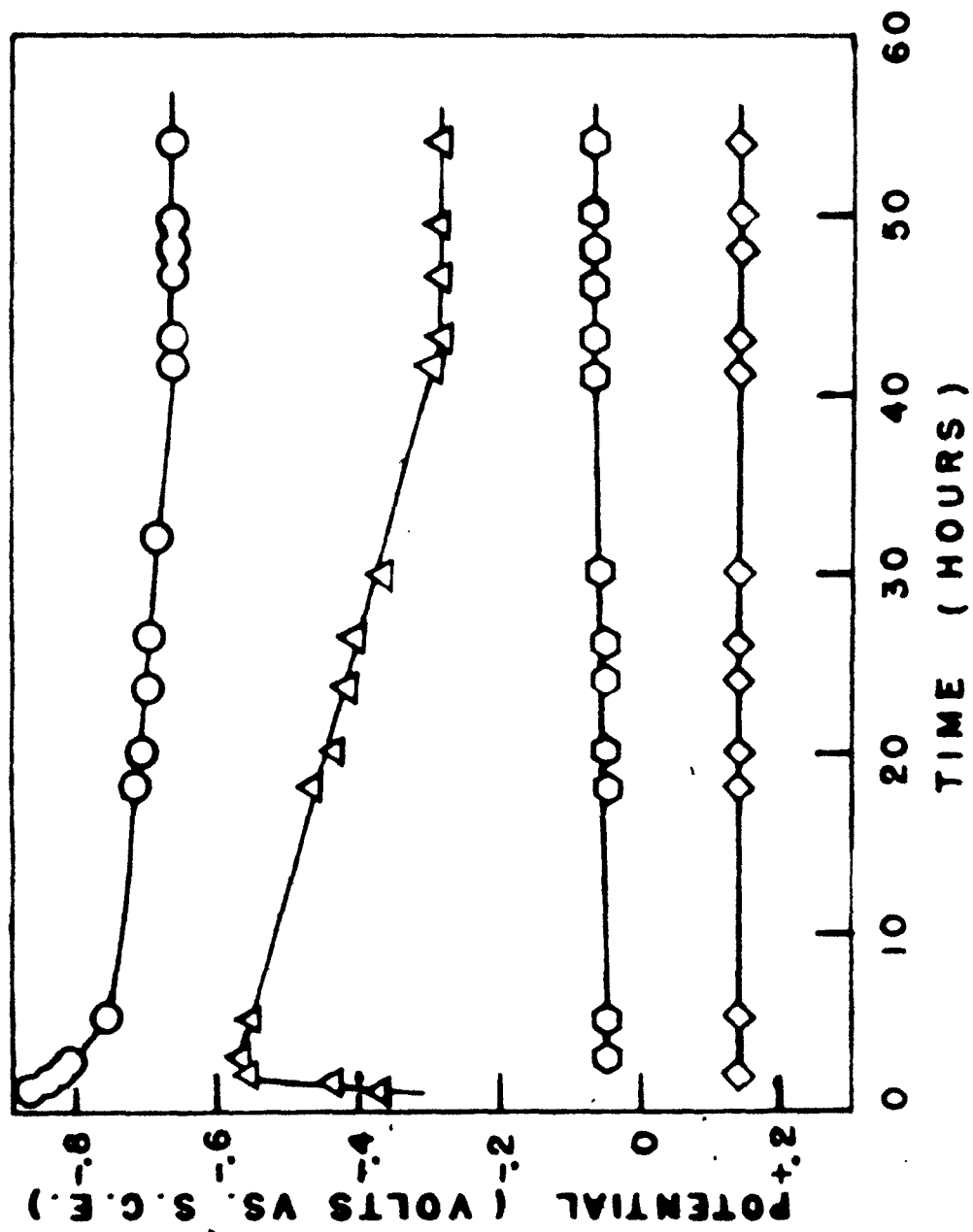
FIGURE 4

The anodic polarization of zirconium in air saturated distilled
water at 40°C.
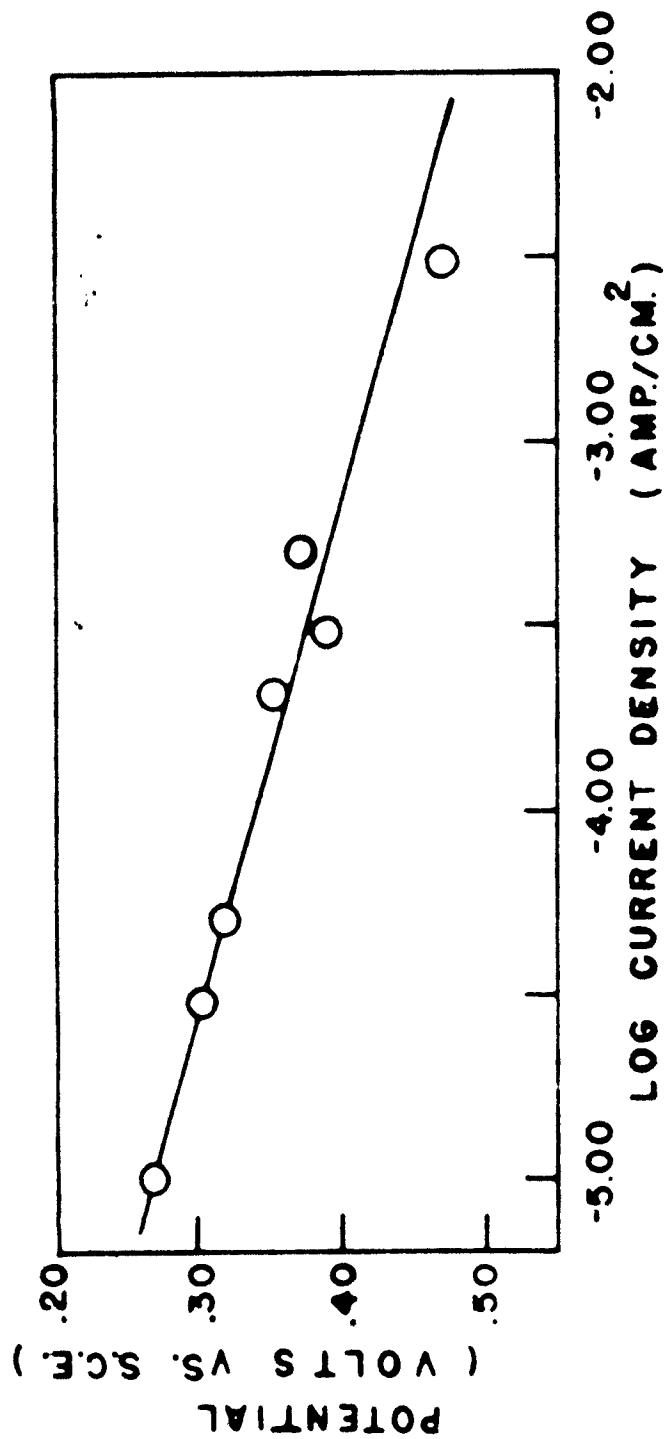
TABLE III

Data for the anodic polarization of zirconium in air
saturated distilled water at 40°C.

Current Density (amp./cm.^{2}.)	Potential (volts vs. S. C. E.)
1.0×10^{-5}	0.27
3.0×10^{-5}	0.30
5.0×10^{-5}	0.32
2.0×10^{-4}	0.35
3.0×10^{-4}	0.39
5.0×10^{-4}	0.37
3.0×10^{-3}	0.47

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When current flow was begun the potential showed a very rapid initial increase to about 0. 1 volt higher than the steady potential, and a subsequent decrease to the constant polarized potential. The initial increase was so rapid that it could not be followed in any of the runs attempted. Continued polarization for several days did not change the potential appreciably.

Examination of the coupon surface after polarization showed a slight amount of pitting and some blackening of the surface.

It was deemed desirable to study the effect of higher temperatures on the anodic polarization curve and the pitting or corrosion of zirconium. The apparatus described earlier and used for the studies thus far described was not suitable for higher temperatures. Therefore, two circular coupons 5. 0 cm.^{2} in area on one face were machined from the same sheet of zirconium. The coupons were scaled in a lucite block with the coupon mold and lucite powder used earlier (1). It was shown that this method of holding the coupon worked well and held up after long use. A 1/8 inch hole was drilled in the back of the block down to the coupon, threaded, and an iron rod threaded on one end, was screwed into the hole. Connection between rod and coupon was insured by a drop of mercury between the two metals. Latex tubing covered the iron rod. The back of the block and tubing were covered with a thick solution of lucite in acetone to prevent water from making contact with the iron at the crack between the latex tubing and the lucite block. The seal made as just described did not break down in boiling water after more than ten hours.

The coupons, thus embedded in lucite, were polished in the usual manner.

It was thought that by using the thermionic amplifier in the circuit a distilled water bridge might be sufficient to furnish contact between the coupon and the saturated calomel electrode. It was not considered practical to use a calomel electrode directly as the agar bridge would melt at higher temperatures and allow chloride ion to diffuse into the solution. The bridge, a length of 8 mm. pyrex glass tubing bent at appropriate places, ran from a 250 ml. beaker containing distilled water at 30°C.and the calomel electrode to an 800 ml. beaker which served as the polarization cell. The tip of the bridge was drawn out into a small capillary.

The coupon was suspended in the 800 ml. beaker by means of the insulated iron rod from a ringstand and the capillary from the distilled water bridge was inserted from behind into a small hole drilled through the center of the lucite and the coupon. The hole had been previously coated with a solution of lucite in acetone and therefore its edges were not exposed to the solution. This type of bridge connection is generally conceded to offer the least disturbance to the current distribution and, as it is very close to the surface, the error due to solution IR drop is at a minimum.

The platinum polarizing electrode was suspended in the beaker from a ringstand and a fritted glass bubbler was placed under the coupon, permitting air to bubble continuously over its surface and to agitate the solution. The cell was kept at a constant temperature by immersing it in a water bath heated with two knife heaters controlled by a bimetallic regulator.

Even with the thermionic amplifier in the circuit the resistance of the distilled water bridge was too high and it was not possible to get potential measurements. However, the two coupons were polarized at 1.0 ma./cm.^{2}, one at 30°C., the other at 87°C. for ten hours each, removed from the solution and their surfaces examined.

At 30°C. a thin, hard, black film had formed unevenly on the electrode surface. The surface had a scaly appearance and a considerable amount of a white, amorphous precipitate was observed in the solution.

At 87°C. the film was again present, darker in appearance than at 30°C., but still unevenly formed. Pitting was noted in the form of many very small pits uniformly distributed over the surface. Scaling of the surface was again observed as was the white, amorphous precipitate which seemed to be present in greater quantity than before.

DISCUSSION

Cathodic Polarization

In general, the cathodic polarization of an inert electrode in a solution such as distilled water is expected to produce a curve with one wave. The reduction of dissolved molecular oxygen to hydroxyl ions, a rapid decrease in potential at the limiting diffusion current of oxygen and the reduction of hydrogen ions to hydrogen gas are the anticipated regions of the curve. The reduction of oxygen occurs at a less negative potential than the reduction of hydrogen ions and therefore occurs at a lower current density.

The curve in Figure 2, however, has two well defined waves. Earlier work on titanium (2) and zirconium in sodium chloride solutions (1) also produced cathodic curves with two waves but the first wave was small, in each case, and some doubt existed concerning its reality. The exact reason this step should be almost twice as large in distilled water is not known.

Earlier, it was stated that the open circuit potential for zirconium in air saturated distilled water at 40°C. is +0.16 volts vs. S. C. E. The open circuit potential determined earlier (1) in 0.5 molar sodium chloride solution was +0.05 volts. In order to check on this difference, one of the runs where the open circuit potential in distilled water was determined was made 0.5 molar in sodium chloride. The potential fell below 0.05 volts, rose above 0.05 volts, and then settled down at that value.

For the cathodic polarization of zirconium in distilled water certain evidence, discussed later, makes it possible to postulate the formation of a zirconium hydride film on the surface of the coupon as the reaction responsible for the first wave. On the basis of this, the linear portion of small slope at low current densities could be explained in the usual way as the reduction of dissolved molecular oxygen to hydroxyl ions, and the first rapid decrease in potential would represent the limiting diffusion current of oxygen. The plateau occurring at a constant potential of -0.30 volts is the region where the hydride film is being formed and the rapid decrease in potential at about 1.0×10^{-4} amp./cm.^{2} is the limiting current density for that reaction. The region of constant decrease in potential at high current density is the hydrogen evolution portion of the curve. The three reactions proposed to explain the curve as then, as follows:

1) $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

2) $H^+ + Zr + e^- \rightarrow ZrH$

3) $H^+ + e^- \rightarrow \frac{1}{2} H_2$

The first and third reactions proposed are acceptable as they are the expected cathodic reactions. As for the second reaction, the formation of a hydride and of a solid solution of hydrogen in zirconium have been reported (3, 4, 5), as has been the cathodic formation of zirconium hydride (6).

It will be recalled that a hard, black adherent film was produced on the zirconium when polarized at current densities along the second plateau and higher, and that the amount of this film increased with increased current density. It was not possible to obtain enough of this film to run an x-ray diffraction pattern on the film by itself so a zirconium coupon which had been polarized at high current density and was well covered with film was placed in a flat plate type powder pack sample holder. The sample was then irradiated with Cu-Kα1 x-rays. A Hayes Type S x-ray diffraction apparatus fitted with an automatically recording goniometer was used. The orientation of the crystals was probably not the most desirable as the sample was not pulverized as is required for best results. Usable data were obtained, however.

Under these conditions lines for both zirconium and the film were obtained, and in order to best distinguish between the two, the coupon was repolished and its diffraction pattern determined. The d spacings and relative intensity values obtained are shown in Table IV along with literature values for zirconium hydride from three sources. It should be borne in mind that because the amount of film was small, the intensity of the zirconium lines should be greater, and as a result the relative intensities of the film lines appear much lower than they would if the film alone had been studied. Several of the zirconium and hydride lines are coincident or lie close together but little, if any, intensity difference is to be expected. The relative intensities in literature references were determined by visual means from a film and hence were subject to variations depending on the judgement of the worker. In this study a geiger type goniometer tube traversed the spectrum and graphically recorded the intensity continuously over the entire spectrum. It was from this graph that the relative intensities were calculated and each number in Table IV is an average of three values, independently determined from different diffraction patterns. For these reasons close agreement between observed and reported relative intensity values cannot be expected.

While this evidence is not absolutely conclusive, it indicates very strongly that the film is a zirconium hydride.

One of the lines (d = 2.95 A$^\circ$) cannot be explained by zirconium or its hydride but is believed to be due to zirconium oxide. Literature values for this line are 2.93(I/I$^\circ$ = 100) (7) and 2.95(I/I$^\circ$ = 70) (8). The intensity of this line is 10%. It would not be unreasonable for a small amount of oxide to be present as the reaction taking place at low current densities is the reduction of oxygen to hydroxyl ions.

Another indication that the formation of a film is the second reaction is given by the cathodic time-potential curves. At currents below the second plateau the potential falls rapidly with time to the constant polarized value. At higher currents, however, a minimum is observed. It is thought that as the potential becomes more negative, hydrogen ions in the solution are reduced and are initially deposited in the atomic state. In this form reaction takes place with the zirconium to form a hydride film and this, essentially, changes the nature of the electrode to that of a zirconium hydride electrode. This should have a potential different from that of a zirconium electrode under the same conditions and so with formation of the film the potential rises to the zirconium hydride potential.

In Figure 2 the slope of the first rapid decrease is considerably more gradual than the slope of the second. This slope is a function of the electron change of the reaction, and on this basis it may be concluded that the electron change in the first reaction is greater than the electron change in the second. If the first reaction is the reduction of molecular

TABLE IV

X-ray diffraction data for zirconium and zirconium plus the black,
adherent, cathodically formed film.

Experimental Values				Literature Values for ZrH (10, 11)					
Zr & Film		Zr				δ-ZrH		ε-ZrH	
d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o
3.06	18	---	---	---	---	---	---	---	---
2.95	10	---	---	---	---	---	---	---	---
---	---	2.80	18	---	---	---	---	---	---
2.75	86	---	---	2.75	100	2.76	100	2.76	100
2.71	72	---	---	---	---	---	---	---	---
2.56	72	2.57	86	---	---	---	---	---	---
2.45	100	2.46	100	---	---	2.49	70	---	---
---	---	---	---	2.38	40	---	---	2.39	70
---	---	---	---	---	---	2.22	50	---	---
2.08	22	---	---	---	---	---	---	---	---
1.89	26	1.89	31	---	---	---	---	---	---
---	---	---	---	---	---	1.76	100	---	---
1.69	16	---	---	1.69	60	1.66	100	1.69	100
1.62	16	1.62	9	---	---	---	---	---	---
1.47	32	1.46	34	1.44	50	1.48	100	1.44	100
1.40	6	---	---	1.38	20	1.38	100	1.38	100
1.36	19	1.37	20	---	---	1.37	100	---	---
1.35	15	1.36	16	---	---	---	---	---	---
1.29	7	1.29	7	---	---	---	---	---	---
---	---	---	---	1.19	50	1.13	100	1.20	50
1.09	11	1.09	7	---	---	---	---	---	---

oxygen to hydroxyl ions then the electron change in the second reaction must be unity. This line of reasoning fits in well with the proposed formation of a hydride film as the second reaction. This same difference in slope may be observed on cathodic curves for zirconium in sodium chloride solution in an earlier work (1), where the reaction proposed was the reduction of a surface film of zirconium oxide which involves a two electron change.

A change in the nature of the electrode surface due to the formation of a hydride film accounts for the hysteresis observed in the region of the first wave and probably involves the reaction of molecular oxygen or hydroxyl ions with the film to form water and zirconium metal.

It was considered more accurate to represent the potentials in the hydrogen evolution portion of the cathodic curve as a function of the current actually involved in the reduction of hydrogen, and consequently the limiting current for the second reaction was subtracted from the current density of each point prior to plotting. The curve in this region is linear with the logarithm of current density and has a slope of -0.135 volts. The potential of the electrode is, then, given by

$$E = -1.84 - 0.14 \log i$$

where E and i are the electrode potential in volts vs. S. C. E. and the current density in amp./cm.^{2}, respectively.

The difference between the reversible and irreversible electrode potentials is the overvoltage and in distilled water (pH 7.0) the reversible hydrogen potential is -0.669 volts vs. S. C. E. The hydrogen overvoltage, therefore, is given by the Tafel equation as

$$\omega = 1.17 + 0.14 \log i$$

where ω and i are the hydrogen overvoltage in volts and the current density in amp./cm.^{2}, respectively. The hydrogen overvoltage at 1 ma./cm.^{2} is 0.75 volts as compared to the earlier value (1) of 0.84 volts in sodium chloride.

Anodic Polarization

On anodic polarization the potential of the zirconium electrode increases linearly with the logarithm of current density through the whole current density range studied. The slope of the line (Figure 4) is 0.07 volts and the potential may be represented as

$$E = 0.62 + 0.07 \log i$$

where E and i are the electrode potential in volts vs. S. C. E. and the current density in amp./cm.^{2}, respectively.

The slight amount of anodic corrosion of zirconium in the absence of electrolyte is somewhat mystifying in view of the passivity and oxide film formation previously observed upon anodic polarization in sodium sulfate solutions (1, 9). Upon addition of sodium sulfate to a cell containing a coupon previously polarized and at equilibrium in distilled water, there was a rapid increase in potential to 15 to 20 volts and the formation of a thick black film. This is in keeping with the earlier work (1, 9).

The small amount of black film formed in distilled water might have been an oxide but it was not possible to determine this with certainty. Sufficient sample could not be obtained for an x-ray diffraction pattern in the conventional manner and application of the same technique used in the hydride study proved unsuccessful.

It is possible that in solutions of sodium sulfate, sulfate ions have a passivating effect on the electrode and, perhaps, enter into the mechanism of oxide film formation.

REFERENCES

1. Norman Hackerman and Olin B. Cecil, Technical Report to the Office of Naval Research on The Electrochemical Polarization of Zirconium in NaCl Solutions, 1 Dec. 1952, under Contract Nonr-375(02) with The University of Texas; also J. Electrochem. Soc., in press.

2. Norman Hackerman and Colby D. Hall, Jr., Technical Report to the Office of Naval Research on The Electrochemical Polarization of Titanium in NaCl Solutions, 1 June 1952, under Contract Nonr-375(02); also J. Phys. Chem., 57, 252 (1953) and J. Electrochem. Soc., in press.

3. M. N. A. Hall, S. L. H. Martin, and A. L. G. Rees, Trans. Faraday Soc., 41, 306 (1945).

4. T. R. P. Gibbs, Jr., J. Electrochem. Soc., 93, 198 (1948).

5. C. G. Moore, D. S. McKinney, and J. C. Warner, USAEC Report NYO-544.

6. C. M. Swartz and M. W. Mallett, USAEC Report AECD 3510.

7. O. Ruff and F. Ebert, Z. anorg. allgem. Chem., 180, 19, (1929).

8. W. M. Cohn and S. Tolksdorf, Z. physik. Chem., B-8, 331 (1930).

9. Pierre Van Ryssleberghe, USAEC Report AECU 2385.

10. A. S. T. M. X-ray Diffraction Data Card No. 2-0862.

11. G. Hagg, Z. physik. Chem., B11, 433 (1930).

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